Spin-spiral inhomogeneity as the origin of ferroelectricity in orthorhombic manganites

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(Dated: September 30, 2010)

We argue that the homogeneous distribution of spins in the spin-spiral state of orthorhombic manganites is deformed by the relativistic spin-orbit interaction. The thus induced spin-spiral inhomogeneity gives rise to the ferroelectric response of the purely electronic origin in even-periodic magnetic structures. The mechanism is generic and explains the appearance of ferroelectricity in the twofold periodic structure of $HoMnO_3$ as well as the fourfold periodic structure of $TbMnO_3$. Nevertheless, odd-periodic magnetic structures preserve the inversion symmetry and thus are not ferroelectric. Our analysis is based on the low-energy model derived from the first-principles electronic structure calculations and the Berry-phase formalism for the electronic polarization.

The possibility of switching the electric polarization **P** by means of magnetic field and the spin magnetization by means of electric field has attracted enormous attention to multiferroic materials because of their potential applicability in new electronic devises as well as the fundamental interest to the problem of coupling between magnetic and electronic degrees of freedom [1]. The orthorhombic rare-earth manganites $R\mathrm{MnO_3}$ (the space group $Pbnm$) are regarded as the key materials for understanding details of such coupling. After discovering the switching phenomena in $TbMnO_3$ [2], an unprecedented number of investigations has been carried out in order to clarify magnetic, structural, and ferroelectric properties of various $R\mathrm{MnO_3}$ compounds (e.g., Refs. [3–5]).

All of them are *improper* ferroelectrics, where the inversion symmetry is broken due to some complex magnetic ordering [1]. Since the Mn-atoms in the $Pbnm$ structure occupy the inversion centers, the latter can be destroyed only if the magnetic unit is larger than the crystallographic one. There are two types of compounds with different periodicity, which are typically regarded as representatives of two main theories of ferroelectricity in $R\mathrm{MnO_3}$. The first one is (nearly) fourfold periodic $TbMnO_3$, where the ferroelectric activity is believed to be due to the spin-orbit interaction (SOI) related spiral spin alignment [6]. Another one is twofold periodic $HoMnO_3$, where **P** is typically ascribed to the (independent on the SOI) magnetostriction effect in the noncentrosymmetric E-type antiferromagnetic (AFM) structure [7].

Nevertheless, many questions remain. (1) There is no unique theory of multiferroicity in $R\mathrm{MnO_3}$. Do $HoMnO_3$ and $TbMnO_3$ really behave as completely different systems, where the ferroelectricity is caused by different microscopic mechanisms? Is it possible to unify these two cases? (2) When the temperature decreases, many spin-spiral manganites, including $TbMnO_3$, exhibit a lock-in transition into a fourfold periodic commensurate phase [3]. What is the origin of these commensurability? Is it different from the twofold periodicity in $HoMnO_3$? (3) The experimental magnetic structure, derived for $TbMnO_3$ and some related compounds by assuming the "spin-spiral" model, rises many questions: even at low temperature, in order to fit the experimental data, one had to rely on the elliptical deformation of the spin spiral [4]. However, in the elliptical distribution, the magnetic moments at certain Mn-sites are substantially reduced (up to about $3\mu_B$ [4]), which clearly contradicts to the Hund's rule physics. Thus, the spin-spiral model is probably incomplete. If so, what is the true magnetic ground state of $R\mathrm{MnO_3}$ and how is it related to the ferroelectric activity of these systems?

In this work we will rationalize some of these questions. We will argue that the ground state of $R\mathrm{MnO_3}$ is *not* the spin spiral. Instead, we will introduce the concept of the *inhomogeneous* spin-spiral, where the inhomogeneity is driven by the relativistic SOI and is actually responsible for the ferroelectric activity in $R\mathrm{MnO_3}$. We will argue that this concept is applicable to all even-periodic systems, including $TbMnO_3$ and $HoMnO_3$.

The magnetic properties of manganites can be linked to the electronic structure of the Mn3d-bands located near the Fermi level. Thus, these bands, after the transformation to the real space, can serve as the Wannier-basis for an effective low-energy model. For $R\mathrm{MnO_3}$ this basis includes three t_{2g} and two e_g orbitals per spin for each of the four Mn-sites in the unit cell. The model Hamiltonian is taken in the Hubbard form, where all the parameters, such as the crystal field, SOI, transfer integrals, and the effective Coulomb interactions are calculated rigorously by starting from the local-density approximation (LDA) and using the experimental crystal structure [8]. The rare-earth $4f$ states are treated as the core, which does not contribute to the low-energy properties. The details of the computational procedure can be found in the review article [9]. The results of such calculations for the whole series of the $R\mathrm{MnO_3}$ compounds without SOI have been reported in Ref. [10]. Here, we only emphasize two points, which are important for the magnetic inversion symmetry breaking: (1) the Jahn-Teller distortion (JTD) gives rise to the large ($\sim$1.5 eV) crystal-field splitting between e_g levels, which manifests itself in the orbital ordering (Fig. 1); (2) The on-site Coulomb repulsion U is not particularly strong ($\sim$2.2 eV) due to the very efficient screening by the O2p band [10], which is im-

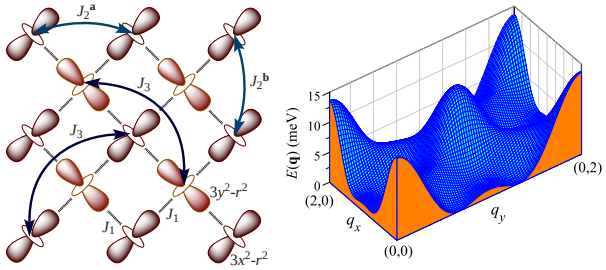

FIG. 1. (Color online) Left panel: schematic view on the orbital ordering and magnetic interactions in the **ab**-plane of RMnO$_3$. Typical values of magnetic interactions for TbMnO$_3$ are J_1= −3.7, $J_2^{\mathbf{a}}$= −0.2, $J_2^{\mathbf{b}}$= −1.2, and J_3= −2.3 meV [10, 11]. Rigt panel: dependence of the total energy (per one Mn atom) on the uniform spin-spiral vector $\mathbf{q} = (q_x, q_y, 1)$ obtained in the HF calculations for TbMnO$_3$ without SOI.

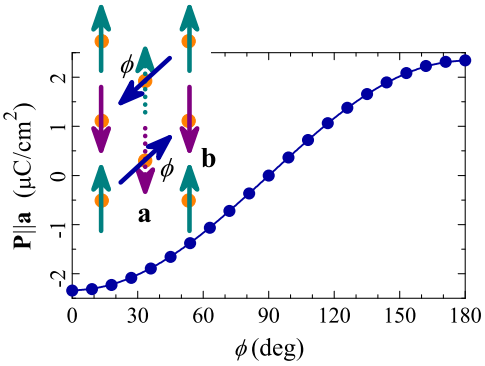

FIG. 2. (Color online) Nonrelativistic electronic polarization for the general periodic q_y=$\frac{1}{2}$ structure of TbMnO$_3$ depending on the angle ϕ between spin magnetic moments in two Mn-sublattices. Relative directions of spins in the **ab** plane are explained in the inset. The numerical value of $|\mathbf{P}|$ in the E-state (ϕ= 0° and 180°) of TbMnO$_3$ is 2.3 μC/cm^2 (and 2.7 μC/cm^2 in the E-state of HoMnO$_3$).

portant for the "right" balance between nearest-neighbor (NN) and some longer-range (LR) magnetic interactions, whose form is controlled by the JTD [10, 11].

Besides JTD, the NN interactions in the **ab**-plane depend on the buckling of the Mn-O-Mn bonds. In the least distorted LaMnO$_3$, J_1 is ferromagnetic (FM) [10, 12]. However, as the hybridization between t_{2g} and e_g states increases in the more distorted compounds, J_1 can become AFM [10]. Since the on-site Coulomb repulsion is not particularly strong, besides conventional superexchange, there are other interactions, which appear in the higher orders of $1/U$, connect more remote sites, and compete with J_1. Among them, the third-neighbor interaction J_3, operating via unoccupied e_g states of intermediate Mn-sites, is the strongest one. The second-neighbor interactions $J_2^{\mathbf{a}}$ and $J_2^{\mathbf{b}}$ are weaker. Nevertheless, what important is the anisotropy $|J_2^{\mathbf{b}}| \gg |J_2^{\mathbf{a}}|$, which predetermines the direction of propagation (**b**) of the spin-spiral and the AFM E-state [10]. The NN interactions between adjacent **ab**-planes are strongly AFM (about −8 meV). The numerical values of J's for TbMnO$_3$ are listed in Fig. 1. Similar behavior was found for HoMnO$_3$ [10].

Without SOI, the competition of isotropic interactions in the **ab**-plane gives rise to the incommensurate spin-spiral state (Fig. 1), which can be obtained by applying the generalized Bloch theorem [13] and solving the model in the Hartree-Fock (HF) approximation [14]. Due to the AFM interactions between the planes, the spin-spiral vector **q**, which specifies the phase $\varphi_{\mathbf{R}}^{\boldsymbol{\tau}} = \mathbf{q}\cdot(\boldsymbol{\tau}+\mathbf{R}) + \alpha^{\boldsymbol{\tau}}$ of the direction of spin $\mathbf{e}_{\mathbf{R}}^{\boldsymbol{\tau}} = (\cos\varphi_{\mathbf{R}}^{\boldsymbol{\tau}}, \sin\varphi_{\mathbf{R}}^{\boldsymbol{\tau}}, 0)$ at the Mn-site $\boldsymbol{\tau}$ of the unit cell **R**, can be searched in the form $\mathbf{q}$=$(q_x, q_y, 1)$, in units of reciprocal lattice translations. The total-energy minimum corresponds to the homogeneous ($\alpha^{\boldsymbol{\tau}}$=0) propagation along the orthorhombic **b**-axis with q_y=0.68 for TbMnO$_3$ (and q_y=0.72 for HoMnO$_3$), which exceeds the experimental values q_y=0.28 and 0.25, reported for the **bc** [2] and **ab** [3] helix, respectively. This discrepancy will be resolved later by considering the relativistic SOI, but first we turn to the analysis of the electronic polarization, which is believed to be closely related to the spin-spiral alignment [6]. For these purposes we compute **P** from the HF eigenvectors $|C_{n\mathbf{k}}\rangle$ in the Wannier-basis by using the Berry-phase formalism on the discrete grid of **k**-points [15]. Since the Wannier-basis (and the model itself) was constructed by starting from the LDA bandstructure, which respects the inversion symmetry, it does not contribute to **P**. The details can be found in Ref. [16]. First, we confirmed that without SOI, the homogeneous spin-spiral state does not produce the electronic polarization. A finite **P** can be indeed obtained by switching on the relativistic SOI and performing one iteration by starting from the self-consistent nonrelativistic HF potential. As a test example, let us consider the q_y=$\frac{1}{3}$ spiral in TbMnO$_3$, which was intensively discussed in the literature [17]. Then, for the **bc** and **ab** helix structure, we obtain $\mathbf{P}||\mathbf{c} \sim 3$ μC/m^2 and $\mathbf{P}||\mathbf{a} \sim 470$ μC/m^2, respectively. Thus, we confirm that our minimal model successfully reproduces results of the first-principles LDA+U calculations for the spin-spiral state [17]: (1) the inequality $\mathbf{P}||\mathbf{a} \gg \mathbf{P}||\mathbf{c}$, which holds for the **ab** and **bc** helix structures; (2) the absolute values of **P**, which are not particularly large.

Being encouraged by this good agreement, we turn to the central part of our work, where we will show that (1) the homogeneous spin-spiral state in RMnO$_3$ is *magnetically* unstable as it tends to deform to some new *inhomogeneous* state under the SOI; (2) this inhomogeneity gives rise to the new *electronic* contribution to **P**.

The simplest example, which illustrates how the ferroelectricity can be induced by the spin-spiral inhomogeneity *without* SOI is the general q_y=$\frac{1}{2}$ periodic structure (Fig. 2). In this case one can realize the collinear (and in-

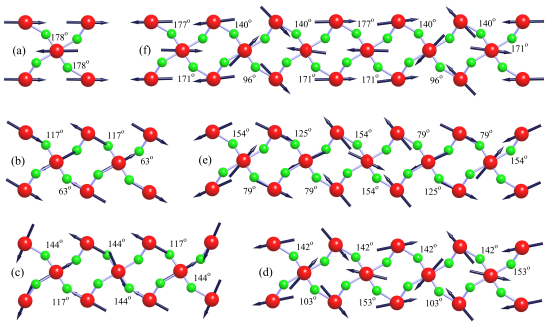

FIG. 3. (Color online) Spin patterns in the **ab** plane of $TbMnO_3$ obtained in the HF calculations with SOI for q_y=1 (a), $\frac{1}{2}$ (b), $\frac{1}{3}$ (c), $\frac{1}{4}$ (d), $\frac{1}{5}$ (e), and $\frac{1}{6}$ (f). The numbers indicate the angles between Mn-spins in different Mn-O-Mn bonds along the orthorhombic **b** axis.

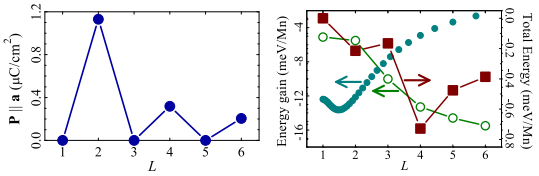

FIG. 4. Left panel: electronic polarization in $TbMnO_3$ depending on the size of the magnetic unit cell L. Right panel: dependence of the total energy on L=1/q_y for the homogeneous spin-spiral states of $TbMnO_3$ without SOI (filled circles), stabilization energy (ΔE) caused by the SOI-induced magnetic relaxation (open circles), and total energies for magnetic superstructures shown in Fig. 3 (squares).

homogeneous in the sense that it is characterized by two magnetically different Mn-O-Mn bonds) E-state and the homogeneous spin-spiral state, depending on the angle ϕ between two Mn-sublattices in the **ab**-plane: ϕ=0 and 180° give rise to two E-phase domains with opposite polarization, while ϕ=90° corresponds to the homogeneous spin-spiral structure with zero net polarization. Thus, in order to obtain finite **P**, it is sufficient to "perturb" the homogeneous spin-spiral state in the direction of the inhomogeneous E-state. For the collinear E-state this mechanism was proposed by Sergienko *et al.* [7]. Then, Picozzi *et al.* considered the behavior of polarization for the more general noncollinear alignment and on the basis of first-principles calculations argued that there is a large electronic contribution to **P** [18], which is semiquantitatively reproduced by our model calculations in Fig. 2.

Now the question is how to stabilize this inhomogeneous spin-spiral structure? One possibility is of course the nonrelativistic exchange striction, which leads to the off-centrosymmetric atomic displacements and stabilizes the AFM E-state [7, 18]. We will come back to the analysis of relative roles played by different mechanisms at the end of the paper, but first we want to show that the inhomogeneous magnetic structure, which gives rise to the finite ferroelectric polarization, can be naturally stabilized by the relativistic SOI. This mechanism is very generic and takes place in the twofold periodic $HoMnO_3$ as well as fourfold periodic $TbMnO_3$. Since the generalized Bloch theorem is no longer valid in the relativistic case, we consider the supercell geometries corresponding to q_y=1/L for which we start from the homogeneous spin-spiral state, turn on SOI and further iterate the HF equations until self-consistency. Typically, this procedure requires several tens of thousands of iterations, which are accompanied by the decrease of the total energy. The results of such calculations for $TbMnO_3$ are summarized in Fig. 3. The equilibrium magnetic structures are characterized by an alternation of the angles formed by spins in different Mn-O-Mn bonds, which indicates the inhomogeneity. The obtained spin patterns reflect the competition of many interactions in the system: the isotropic interactions tend to form the uniform spin spiral, while relativistic SOI, which couples spin magnetic moments to the lattice, tends to restore the commensurability in the system. The magnetic moments lie mainly in the **ab**-plane (apart from small canting in the **c**-direction) [19]. The q_y=1 structure is mainly formed by the NN interactions and the magnetic anisotropy [12], while the LR interactions are not affective due to the periodicity constraint. For the q_y=$\frac{1}{2}$ structure, the spins are aligned parallel to the longest Mn-O bonds and minimize the single-ion anisotropy energy. Moreover, the magnetic coupling along the **b**-axis minimizes the energy of LR interactions. For the large-L structures, the situation is even more complex: certain spins minimize the single-ion anisotropy energy, while the directions of other spins compromise between NN, LR, and relativistic anisotropic and Dzyaloshinsky-Moriya interactions. For the q_y=$\frac{1}{6}$ structure one can clearly distinguish different "domains" formed by the NN interactions and the single-ion anisotropy, respectively. Most importantly, all odd-periodic magnetic structures restore the inversion centers (associated with the central Mn-sites in Fig. 3) and thus exclude any ferroelectric activity.

Thus, we predict the oscillatory behavior of **P** depending on q_y=1/L (Fig. 4). The spin-spiral inhomogeneity in the even-periodic structures gives rise to the electronic polarization, similar to the E-state, which decreases with the increase of L. The canting of spins away from the collinear arrangement substantially reduces the values of **P**. For example, the electronic polarization |**P**|= 1.1 μC/cm^2, obtained for the q_y=$\frac{1}{2}$ structure of $TbMnO_3$ (Fig. 4), is reduced by factor two in comparison with the collinear E-state (Fig. 2). Taking into account the numerical values of ϕ (Fig. 3), this reduction is readily explained by the angle-dependence of **P** in the nonrelativistic case (Fig. 2). Thus, the SOI only forms the

inhomogeneous spin-spiral state, while the microscopic mechanism yielding finite **P** is essentially nonrelativistic.

The existing theories overestimate the values of **P** (sometimes by an order of magnitude) [7, 18], which is one of the unresolved problems for the multiferroic manganies. In our calculations we obtain **P**||**a**= 1.4 μC/cm^2 for the q_y=$\frac{1}{2}$ structure of $HoMnO_3$ (ϕ=120°) and 0.3 μC/cm^2 for the q_y=$\frac{1}{4}$ structure of $TbMnO_3$ shown in Fig. 4. Both values are about three times larger than the experimental ones [5]. Nevertheless, our theoretical approach also suggests that it is difficult to obtain a good quantitative agreement because **P** is sensitive to many factors: (1) the precise value of ϕ, which itself depends on the fragile balance of many magnetic interactions; (2) structural relaxation [7, 18]; (3) due to the oscillatory behavior (Fig. 4), **P** can be reduced by possible deviations from the even-periodic commensurate alignment.

Finally, we comment on the relative roles played by the magnetic and structural relaxation effects in the formation of inhomogeneous magnetic structures. The behavior of the magnetic stabilization energies ΔE, defined as the energy difference between fully optimized magnetic structure with SOI and the homogeneous spin-spiral state without SOI, is explained in Fig. 4. Since each increase of the supercell provides additional degrees of freedom for the magnetic relaxation, ΔE decreases with the increase of L. The absolute value $|\Delta E|\sim$6 meV/Mn obtained for the q_y=$\frac{1}{2}$ structure of $HoMnO_3$ is comparable with the energy gain caused by noncentrosymmetric atomic displacements in the E-state ($\sim$8 meV/Mn [18]). Thus, even for q_y=$\frac{1}{2}$, the magnetic relaxation cannot be neglected and should be considered on an equal footing with the structural relaxation. Moreover, the transition to the inhomogeneous state is driven by the SOI, prior to structural relaxation, and in this sense there is no conceptual difference between $HoMnO_3$ and $TbMnO_3$. Since $|\Delta E|$ increases with L, the relative role of the magnetic relaxation is also expected to increase. The magnetic relaxation alone readily explains the experimentally observed $q_y\approx\frac{1}{4}$ periodicity in $TbMnO_3$: ΔE of the relativistic origin shifts the total energy minimum of the homogeneous spin-spiral state (q_y=0.68, Fig. 1) towards smaller q_y. Thus, the new theoretical minimum corresponds to q_y=$\frac{1}{4}$ (Fig. 4). Similar behavior was found for $HoMnO_3$, which is expected to form similar fourfold periodic structure. The disagreement with the experimentally observed twofold periodicity in $HoMnO_3$ is probably caused by the neglect of the structural relaxation, which is relatively more important for q_y=$\frac{1}{2}$. Quantitative aspects of interplay between magnetic and structural relaxation effects should be addressed in future theoretical studies. At present, the structural relaxation cannot be easily implemented in the present model analysis.

In summary, we propose that the homogeneous spin-spiral state in orthorhombic manganites is deformed by the relativistic SOI. The thus induced inhomogeneity is responsible for the ferroelectric activity of RMnO$_3$. It would be interesting to check our finding experimentally.

This work is partly supported by Grant-in-Aid for Scientific Research (C) No. 20540337 from the Ministry of Education, Culture, Sport, Science and Technology of Japan and by Russian Federal Agency for Science and Innovations, grant No. 02.740.11.0217.

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planar structure minimizes the anisotropy energy in the Mn-sublattice, while the **bc**-planar structures are probably stabilized by the magnetism of the R-ions [5], which is not considered in the present work.